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(54) Title: IN SITU DEHYDROXYLATION OF SUPPORTS AND PREPARATION OF SUPPORTED METALLOCENE POLYOLEFIN CATALYSTS (57) Abstract The present invention provides a method to prepare, <i>in situ</i> , a supported metallocene catalyst precursor on a dehydroxylated support. The method comprises the following steps: (A) reacting reagents (i), (ii) and (iii) in the presence or absence of a solvent, wherein (i) is a compound that is a transitional metal or rare earth metals compound; (ii) is a metal containing reagent, wherein the metal component or the reagent is selected from the group consisting of tin, silicon, germanium and mixtures thereof and the remaining component of the reagent contains a five-member carbon ring, a heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi cyclic moieties capable of coordinating to the transition or rare earth metals; and (iii) is a hydroxyl group containing support materials; (B) recovering the resulting supported catalyst precursor.		

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INSITU DEHYDROXYLATION OF SUPPORTS AND
PREPARATION OF SUPPORTED METALLOCENE POLYOLEFIN CATALYSTS

This application is a continuation-in-part of U.S.
Patent Application Serial No. 08/331,439, filed on October
31, 1994.

Background

5 It has been known to use metallocene compounds of
transition metals as catalysts for polymerization and
copolymerization of olefins.

10 The use of metallocene catalyst systems provides the
ability to produce uniform polymers and copolymers of
narrow molecular weight distribution (MWD) and narrow
compositional distribution.

15 Solution, slurry, and gas phase polymerization
techniques are well known in the field. See, e.g.,
Krichelderf, Handbook of Polymer Synthesis, Chapter 1,
Part A, p.7-8 (Marcel Dekker 1992). However, in order to
use the metallocene catalyst effectively, the active
catalytic specie needs to be supported. There are known
supports and known means by which to place the
metallocene active specie on the support. These means
20 involve physically adding the metallocene to the support
after the catalyst is prepared. This merely physically
combines the active specie with the support.

 A drawback to the use of supported metallocene
catalysts is that many oxide supports contain active

hydroxyl groups. These hydroxyl groups are reactive and tend to deactivate the active, expensive metallocene specie. Accordingly, it is often desirable to deactivate the hydroxyl groups.

5 In the past, various chemical and/or thermal treatments have been used in an effort to achieve dehydroxylation of the oxide support particles.

10 Thermal treatments (i.e., calcining) have been used and are advantageous in that they do not add undesirable chemicals to the support and that they are relatively simple, inexpensive processes. Unfortunately, thermal treatments are often ineffective for achieving a high degree of dehydroxylation. Further, for many porous oxide supports (e.g., silica gel), thermal treatments
15 often result in an undesirable loss of pore volume, shrinkage of the pores and/or loss of surface area.

 Chemical treatments have been attempted. Many types of chemicals have been used such as organo aluminum compounds, magnesium chloride/dehydrating agents
20 combinations, organosilanes, halosilanes, silanes, etc. These various chemical processes are often expensive and may result in the addition of undesired or complicating constituents to the oxide support.

Thus there remains a need for improved techniques to support metallocene catalytic species while deactivating the hydroxyl groups present on oxide support materials and avoiding the problems of having undesired chemical constituents or thermal effects.

Accordingly, it is an object of the present invention to provide novel methods for making supported metallocene precursors in-situ wherein hydroxyl groups are deactivated.

Additionally, another object of the present invention is to provide a catalyst which is capable of producing polymer with a broad molecular weight.

These and other objects are accomplished by a catalyst produced by the presently disclosed "in-situ method" of catalyst preparation as described below and using the present catalyst in solution, slurry and gas phase polymerization processes to obtain desirable novel polymers.

4

Summary of the Present Invention

In accordance with one aspect of the present invention, there is provided a novel composition of matter useful as polyolefin catalyst.

5 Also provided in accordance with this invention are methods of making and using the novel compositions to polymerize olefins.

10 The invention further provides unique catalyst compositions suitable for forming polymers having broad molecular weight distribution and good flow properties (i.e., the ability to be processed through dies and other machinery without raising the processing temperature or pressure). The polymers produced in accordance with the present invention also have reduced presence of polymer
15 degrading and equipment corroding materials, such as chlorine, in the final polymer product.

20 The present invention provides a method to prepare, in-situ, a supported metallocene catalyst precursor on a dehydroxylated support. The method comprises the following steps:

(A) reacting reagents (i), (ii) and (iii) in the presence or absence of a solvent, wherein

(i) is a compound that is a transition metal compound, optionally containing a five-member carbon

ring, a heterosubstituted five-member carbon ring,
or a bridged (ansa) ligand defined as multi- cyclic
moieties capable of coordinating to the transition
or rare earth metals;

5 (ii) is a metal containing reagent, wherein the
metal component of the reagent is selected from the group
consisting of tin, silicon, germanium and mixtures
thereof and the remaining component of the reagent is
selected from the group of halogen elements, organics,
10 amides and mixtures thereof, and optionally, containing
an additional organic component that contains a five-
member carbon ring, a heterosubstituted five-member
carbon ring, or be a bridged (ansa) ligand defined as
multit-cyclic moieties capable of coordinating to the
15 transition or rare earth metals; and

(iii) is a hydroxyl group containing support
material;

(B) recovering the resulting supported catalyst
precursor.

20

Detailed Description of the Invention

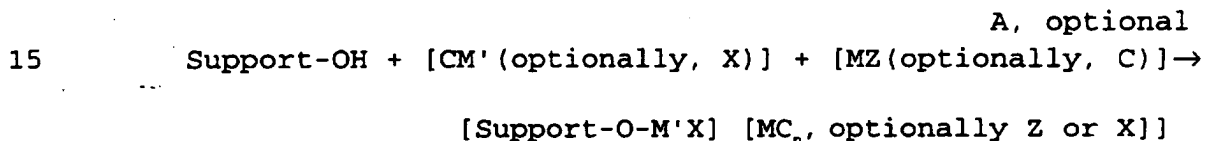
Catalyst precursors of the present invention are
useful in the polymerization of any olefin in which
separate polymerization with a homogeneous catalyst or
with a heterogeneous catalyst is possible. Preferably,

6

5 The catalyst precursors produced according to the present invention are described below in terms of the manner in which they are made.

The method to prepare supported catalyst precursors according to the present invention can be described by the following graphic representations.

Illustration I (InSitu Preparation and Dehydroxylation)



20 The terms used in Illustration I are defined below.

Support

The Support can be any sufficiently porous inorganic, inorganic oxides and organic materials containing hydroxyl groups. Suitable inorganic materials include magnesium compounds or their complex salts such as $MgCl(OH)$ and $Mg(OH)_2$. Inorganic oxide supports, include talcs, clays, and metal oxides from Groups 2-14,

actinide, lanthanide Series metals from the Periodic Table; suitable metal oxides are typically SiO_2 , Al_2O_3 , MgO , ZrO_2 , Fe_2O_3 , B_2O_3 , CaO , ZnO , BaO , ThO_2 and mixtures thereof; for example, silica-alumina, silica-titania, silica-titania-alumina, zeolite, ferrite, glass fibers, magnesia, titania, zirconia, aluminum phosphate gel and mixtures thereof

Organic Supports include resinous material such as polyvinylalcohol, starches and mixtures thereof.

Preferably, the supports are compositions conventionally used as catalyst support materials. The degree of porosity in the carrier may be any level that is achievable in the starting material. Preferably, the carrier particles of the present invention have a pore volume of at least 0.1 cc/g; preferably more than 1.0 cc/g; and more preferably from about 0.3 to 5 cm^3/g . Preferably, the carrier particles have a surface area of about 1-1000 m^2/g ; more preferably in the range of from 100 - 800 m^2/g ; and more preferably 250-600 m^2/g . The typical median particle size for a suitable carrier for this invention is from 1 to 300 microns, preferably from 5 to 200 microns and more preferably from 25 to 150 microns.

Pore volume and surface area, for example, can be measured from volume of nitrogen gas adsorbed in accordance with BET method. (Refer to J. Am. Chem. Soc., Vol. 60, p. 309 (1983)).

5 C

C represents a ligand defined as one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi-cyclic moieties capable of coordinating to the transition or
10 rare earth metals, M.

The ansa bridge can be selected from the group comprising carbon, silicon, phosphorus, sulfur, oxygen, nitrogen, germanium, species such as R''_2C , R''_2Si , R''_2Ge , $R''_2CR''_2C$, $R''_2SiR''_2Si$, $R''_2GeR''_2Ge$, $R''_2CR''_2Si$, $R''_2CR''_2Ge$,
15 $R''_2CR''_2CR''_2C$, $R''_2SiR''_2Si$, diradicals where R is independently selected from the group containing hydride, halogen radicals, and C1-20 hydrocarbyl radicals including ethyl, propyl; preferred ansa bridges are Me_2Si (dimethylsilyl), Ph_2Si (diphenylsilyl), Me_2C (isopropylidene), Ph_2P (diphenylphosphoryl) $Me_2SiSiMe_2$
20 (tetramethyldisilane) and the like. Preferably, the ansa bridge has a length of two atoms or less as in methylene, ethylene, diphenysilyl, dimethylsilyl, and methylphenylsilyl.

9

M'

M' represents a metal selected from the group comprising silicon, tin, germanium and mixtures thereof.

5

M

M represents a metal selected from the group consisting of Groups 3 through 10, lanthanides, actinides metals of the Periodic Table and mixtures thereof; preferably titanium, zirconium, hafnium, chromium, vanadium, samarium, neodymium and mixtures thereof; most preferably Ti, Zr, and Hf, and mixtures thereof.

10

The definition of MZ is intended to include any existing Ziegler-Natta catalytic precursors.

15

X and Z

X and Z represents elements from the halogen group (preferably chlorine, fluorine, bromine and mixtures thereof); and substituted and nonsubstituted alkoxys (preferably C1-C20 alkoxys, such as methoxy, ethoxy, isopropoxy, butoxy and phenoxy); alkyls (preferably C1-C20 alkyls such as ethyl, butyl, octyl, ethylhexyl); aryls (preferably C6-C20 aryls such as phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl);

20

alkenyls (preferably C1-C20 alkenyls, such as ethenyl, propenyl, butenyl, pentenyl); amides (preferably NR^aR^b , wherein the R^a and R^b can be the same or different and independently selected from alkyls, alkenyls, aryls, or silanes; preferably C1-C20 alkyls and alkenyls and C6-C20 aryls, including substituted aryls, such as ethyl, butyl, octyl, ethylhexyl), phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl); and preferred R groups in the NR^aR^b are C1-C5 alkyls, C2-C5 alkenyls, phenyl and naphthyl and mixtures thereof.

Preferred amides are dimethylamide, diethylamide, hexamethyldisilazide and mixtures of two or more of the foregoing.

PREFERRED CM'X

CM'X is preferably selected from the group comprising (chlorodimethylsilyl)(3-trimethylsilyl) cyclopentadiene, cyclopentadienyltrimethylsilane, indenyltrimethylsilane, indenyltributylstannane, indenyltrimethylgermanium, cyclopentadienyl trimethylgermanium, and mixtures thereof.

//

A

A, may be optionally used to further modify the catalyst and/or support, and can be selected from the group comprising acid halides, (e.g., HCl, HBr and HI); metal halides (preferably, Al, Si, Sn, Ti, Mg, Cr and mixtures thereof, wherein the halide are Cl, Br, I and mixtures thereof; organic halides (R'X), carboxylic acids (R'(COOH)_n), esters (R'(COOR'')_n), ethers (R'(OR'')_n) when n is equal to or greater than 1, alcohols wherein the R' and R'' are the same or different and independently selected from mono or multi-cyclic, halosubstituted and non-substituted aryls, alkyls, and alkenyl groups and mixtures thereof; preferred are C1-20 alkenyl groups (such as ethene, propylene, butene, and pentene); C1-20 alkyl groups (such as a methyl, ethyl, n-propyl, isopropyl, n-butyl, n-octyl, and 2-ethylhexyl groups), C6-20 aryl group (including substituted aryls) (such as phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6 dimethylphenyl, 3,5- methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl groups) and mixtures thereof. More preferred R groups are C1-5 alkyls, C2-5 alkenyls phenyl and naphthyl and mixtures thereof.

"A" can also be C1-C20 alkylaluminums (preferably C1-C10 alkyl aluminums, and most preferably triethyl

aluminum, trimethylaluminum, tributylaluminum and mixtures thereof); C1-C20 alkyl lithium (preferably, C1-C6 alkyl lithiums, and most preferably n-butyllithium, methyllithium, ethyllithium and mixtures thereof); and
5 Grignard reagents, generally represented by the formula $RMgX$, where X is selected from the members of the halogen group from the Periodic Table, R is selected from the group comprising a C1-C20 alkyls and C6-C20 aryls, preferably C1-C6 alkyls and C6-C10 aryls; preferred
10 Grignard reagents are methyl magnesium chloride, ethyl magnesium chloride, and isopropyl magnesium bromide and mixtures thereof.

Additional suitable "A" compounds for use in this invention is selected from the halogen gases and C1-C5
15 alkyl alumoxanes such as methylalumoxane, isobutylalumoxane and mixtures thereof.

Preferred A's include CH_3Cl , tetrahydrofuran, t-butylchloride, dialkyl phthalates, ethanol, phenol, ethyl-aluminumdichloride, silicon tetrachloride,
20 methyllithium, methyl magnesium chloride, triethylaluminum, methylalumoxane, dibutylphthalate and tin tetrachloride; halogen gases such as Cl_2 , Fl_2 , and Br_2 and mixtures of two or more of the foregoing.

The reaction can be carried over a broad range of temperatures, typically from approximately -78°C to 200°C, preferably at 0°C to room temperature.

The reaction product will typically have the following compositional characteristics. The values provided below are given in weight percent of the final dry catalyst.

CMZ is approximately 0.1% to 50%; preferably 0.1 - 10; most preferably 0.1-5.0;

M'X is approximately 0.1% to 99.8%; preferably 5.0-50; most preferably 5-15; and

Support is approximately 0.1% to 99.8%.

The reaction described in Illustrations I is carried out in the presence of a solvent in either a solution or a slurry. The solvents that are desirably utilized are solvents that do not adversely affect the preparation of the catalyst or, if any residue remains, does not adversely affect polymerization or the properties of the resulting polymer. Preferably, the solvent is a non-polar organic solvent; and most preferably includes aliphatic hydrocarbons (typically C3 to C12, such as butane, isobutane, pentane, isopentane, hexane, octane, decane, dodecane, hexadecane, octadecane,

14

and the like); alicyclic hydrocarbons (typically C5-C20, such as cyclopentane, methylcyclopentane, cyclohexane, decalin cyclooctane, norbornane, ethylcyclohexane and the like); aromatic hydrocarbons, including substituted aromatics such as benzene, chlorobenzene, xylene, toluene and the like; and petroleum fractions such as gasoline, kerosene, light oils, and the like. It may also be desirable to use tetrahydrofuran or another ether. Mixtures of two or more solvents may also be used, e.g., Exxon's IsoPar ®.

15

PREFERRED PRODUCTS CMZ or CMX

The starting materials can be selected as defined above to achieve the desired CMZ or CMX. Such CMZ or CMX metallocene catalytic precursors are defined as organometallic compounds having a transition metal, including rare earth metals M as defined previously, in coordination with members of at least one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi cyclic moieties capable of coordinating to the transition or rare earth metals.

The ansa bridge can be selected from the group comprising carbon, silicon, phosphorus, sulfur, oxygen, nitrogen, germanium, species such as, R^1_2C , R^1_2Si , R^1_2Ge , $R^1_2CR^1_2C$, $R^1_2SiR^1_2Si$, $R^1_2GeR^1_2Ge$, $R^1_2CR^1_2Si$, $R^1_2CR^1_2Ge$, $R^1_2CR^1_2CR^1_2C$, $R^1_2SiR^1_2Si$ diradicals where R^1 is independently selected from the group containing hydride, halogen radicals, and C1-20 hydrocarbyl radicals including ethyl and propyl; preferred ansa bridges are Me_2Si (dimethylsilyl), Ph_2Si (diphenylsilyl), Me_2C (isopropylidene), Ph_2P (diphenylphosphoryl), $Me_2SiSiMe_2$ (tetramethyldisilane) and the like. Preferably, the ansa bridge has a length of two atoms or less as in methylene, ethylene,

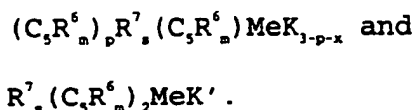
16

diphenylsilyl, dimethylsilyl, propylidene and methylphenylsilyl.

The transition metal component of the metallocene product is selected from Groups 3 through 10, lanthanides and actinides of the Periodic Table and mixtures thereof; and most preferably, titanium, zirconium, hafnium, chromium, vanadium, samarium and neodymium and mixtures thereof. Of these Ti, Zr, and Hf and mixtures thereof are most preferable.

In one preferred embodiment, the CMZ metallocene catalyst precursor product is represented by the general formula $(Cp)_m MR_n^4 R_p^5$, wherein Cp is a substituted or unsubstituted cyclopentadienyl ring, M is a Group 3-6, lanthanide, actinide series metal from the Periodic Table and mixtures thereof; R^4 and R^5 are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; $m=1-3$, $p=0-3$ and the sum of $m+n+p$ equals the oxidation state of M.

In another embodiment the CMX is represented by the formulae:



Wherein Me is a Group 3-6, lanthanide, actinide series metal from the Periodic Table and mixtures

thereof; C_5R^6 is a substituted cyclopentadienyl. each R^6 , which can be the same or different is hydrogen, alkenyl, aryl, or arylalkyl radical having from 1 to 20 carbon atoms or two carbon atoms joined together to form a part of a C4 to C6 ring; R^7 is one or more of or a combination of a carbon, a germanium, a silicon, a phosphorous or a nitrogen atom containing radical substitution on and bridging two C_5R^6 rings or bridging one C_5R^6 ring back to Me, when $p=0$ and $x=1$ otherwise x is always equal to 0, each K which can be the same or different is an aryl alkyl, alkenyl, alkaryl, or arylalkyl radical having from 1-20 carbon atoms or halogen, K' is an alkylidene radical having from 1 to 20 carbon atoms, s is 0 to 1 and when s is 0, m is 5 and p is 0, 1, or 2 and when s is 1, m is 4 and p is 1.

In particular, preferred metallocenes are derivatives of a cyclopentadiene (Cp), including cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, and 1,1-disubstituted silacyclopentadienes, phosphocyclopentadienes, 1-metallocyclopenta-2,4-dienes, bis(indenyl)ethane and mixtures thereof.

Additional illustrative, but non-limiting, examples of metallocenes represented by the above definition are dialkyl metallocenes such as bis(cyclopentadienyl)titanium

dimethyl, bis(cyclopentadienyl)titanium diphenyl,
bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadie
nyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium dimet
hyl and diphenyl, bis(cyclopentadienyl)titanium di-
5 neopentyl,
bis(cyclopentadienyl)zirconium di neopentyl, bis(cyclopent
adienyl)titanium dibenzyl, bis(cyclopentadienyl)zirconium
dibenzyl, bis(cyclopentadienyl)vanadium
dimethyl; the mono alkyl metallocenes such as bis(cyclopen
10 tadienyl)titanium methyl chloride, bis(cyclopentadienyl)ti
tanium ethyl chloride, bis(cyclopentadienyl)titanium
phenyl chloride, bis(cyclopentadienyl)zirconium methyl
chloride,
bis(cyclopentadienyl)zirconium ethyl chloride, bis(cyclope
15 ntadienyl)zirconium phenyl chloride, bis(cyclopentadienyl)
titanium methyl bromide; the trialkyl metallocenes such as
cyclopentadienyl titanium trimethyl, cyclopentadienyl
zirconium triphenyl, and cyclopentadienyl zirconium
trineopentyl, cyclopentadienyl zirconium trimethyl,
20 cyclopentadienyl hafnium triphenyl, cyclopentadienyl
hafnium trineopentyl, and cyclopentadienyl hafnium
trimethyl; monocyclopentadienyls titanocenes such as,

pentamethylcyclopentadienyl titanium trichloride,
pentaethylcyclopentadienyl titanium trichloride;
bis(pentamethylcyclopentadienyl) titanium diphenyl, the
carbene represented by the formula bis(cyclopentadienyl)ti
tanium=CH₂ and derivatives of this reagent; substituted
5 bis(cyclopentadienyl)titanium (IV) compounds such as:
bis(indenyl)titanium diphenyl or dichloride, bis(methylcyc
lopentadienyl)titanium diphenyl or dihalides; dialkyl, tri
-alkyl, tetra-alkyl and penta-alkyl cyclopentadienyl
10 titanium compounds such as bis(1,2-
dimethylcyclopentadienyl)-titanium diphenyl or dichloride,
bis(1,2-diethylcyclopentadienyl)titanium diphenyl or
dichloride; silicon, phosphine, amine or carbon bridged
cyclopentadiene complexes, such as dimethyl silyldicyclope
15 ntadienyl titanium diphenyl or dichloride, methyl
phosphine
dicyclopentadienyl titanium diphenyl or dichloride,
methylenedicyclopentadienyl titanium diphenyl or
dichloride and other dihalide complexes, and the like; as
20 well as
bridged metallocene compounds such as isopropyl(cyclopenta
dienyl)(fluorenyl)zirconium dichloride, isopropyl(cyclopen
tadienyl)(octahydrofluorenyl)zirconium dichloride

- diphenylmethylenecyclopentadienylfluorenyl zirconium
dichloride, diisopropylmethylenecyclopentadienylfluorenyl zirconium dichloride, diisobutylmethylenecyclopentadienylfluorenyl zirconium
- 5 dichloride, ditertbutylmethylenecyclopentadienylfluorenyl zirconium dichloride, cyclohexylidenecyclopentadienylfluorenyl zirconium dichloride, diisopropylmethylenecyclopentadienylfluorenyl zirconium
- 10 dichloride, isopropylcyclopentadienylfluorenyl hafnium dichloride, diphenylmethylenecyclopentadienylfluorenyl hafnium dichloride, diisopropylmethylenecyclopentadienylfluorenyl hafnium dichloride, diisobutylmethylenecyclopentadienylfluorenyl hafnium dichloride,
- 15 ditertbutylmethylenecyclopentadienylfluorenyl hafnium dichloride, cyclohexylidenecyclopentadienylfluorenyl hafnium dichloride, diisopropylmethylenecyclopentadienylfluorenyl hafnium dichloride, isopropylcyclopentadienylfluorenyl titanium
- 20 dichloride, diphenylmethylenecyclopentadienylfluorenyl titanium dichloride, diisopropylmethylenecyclopentadienylfluorenyl titanium dichloride, diisobutylmethylenecyclopentadienylfluorenyl titanium dichloride, ditertbutylmethylenecyclopentadienyl

21

(fluorenyl)titanium dichloride, cyclohexylidene(cyclopentadienyl) (fluorenyl)titanium dichloride,
diisopropylmethylene(2,5 fluorenyl)titanium dichloride,
racemic-ethylene bis (1-indenyl) zirconium (IV)
5 dichloride, racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) zirconium (IV) dichloride, racemic-dimethylsilyl
bis (1-indenyl) zirconium (IV) dichloride, racemic-
dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) zirconium
(IV) dichloride, racemic-1,1,2,2- tetramethylsilanylene
10 bis (1-indenyl) zirconium (IV) dichloride, racemic-
1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl)
zirconium (IV), dichloride, ethylidene (1-indenyl
tetramethylcyclopentadienyl) zirconium (IV) dichloride,
15 racemic- dimethylsilyl bis (2-methyl-4-t-butyl-1-cyclopentadienyl) zirconium (IV) dichloride, racemic-
ethylene bis (1-indenyl) hafnium (IV) dichloride, racemic-
ethylene bis (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV)
dichloride, racemic-dimethylsilyl bis (1-indenyl) hafnium
20 (IV) dichloride, racemic-dimethylsilyl (4,5,6,7-tetrahydro-1-indenyl) hafnium (IV) dichloride, racemic-
1,1,2,2-tetramethylsilanylene bis (1-indenyl) hafnium(IV)
dichloride, racemic-1,1,2,2-tetramethylsilanylene bis

(4,5,6,7-tetrahydro-1-indenyl) hafnium (IV), dichloride, ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-cyclopentadienyl) hafnium (IV) dichloride, racemic-ethylene bis (1-indenyl) titanium (IV) dichloride, 5 racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, racemic- dimethylsilyl bis (1-indenyl) titanium (IV) dichloride, racemic- dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis (1- 10 indenyl) titanium (IV) dichloride racemic-1,1,2,2-tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl) titanium (IV) dichloride, and ethylidene (1-indenyl-2,3,4,5-tetramethyl-1-cyclopentadienyl) titanium IV) dichloride.

15 Preferred CMXs or CMZs are bis(cyclopentadienyl)titanium dichloro, bis(cyclopentadienyl)zirconium, isopropyl(cyclopentadienyl)fluoroenyl)zirconium dichloro, bis (1-indenyl) zirconium (IV) dichloro, (4,5,6,7-tetrahydro-1-indenyl)hafnium(IV)dichloro, 20 dimethylzirconocene, dichloroethylenebisindenylzirconium, and dichloroethylene bis(tetrahydroindenyl)zirconium.

POLYMERIZATION

The catalytic precursors prepared according to the method of the present invention may be activated by any number of catalytic activators and used to polymerize olefinic materials.

5 The catalytic activator includes organometallic compounds. Preferably, the metals are selected from the group including lithium, aluminum, magnesium, zinc and boron. Such catalyst are known for their use in polymerization reactions, especially the polymerization
10 of olefins. These include organo aluminum compounds such as trialkyl, alkyl hydrido, alkylhalo and alkyl alkoxy aluminum compounds. Suitably each alkyl or alkoxy group contains 1-16 carbons. Examples of such compounds include trimethylaluminum, triethylaluminum, diethyl
15 aluminumhydride, triisobutylaluminum, tridecyl aluminum, tridodecylaluminum, diethyl aluminum methoxide, diethyl aluminum ethoxide, diethyl aluminum phenoxide, diethyl aluminum chloride, ethyl aluminum dichloride, methyl diethoxy aluminum and methyaluminoxane. The preferred
20 compound is as an alkyl aluminoxane, the alkyl group having 1 to 10 carbon atoms, especially methyl aluminoxane.

Additional suitable catalytic activators for use with this invention are represented by the formulae:

24

$[C^+][N^+(Q_1-Q_{n-1})]$ and $N^+(Q_n)$.

$[C^+]$ is an activating cation, which may be a Bronsted acid capable of donating a proton to the transition metal ionic catalytic precursor resulting in a transition metal cation. Such Bronsted acids include but are not limited to ammoniums, oxoniums, phosphoniums and mixtures thereof; preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo-N,N-dimethylaniline, p-nitro-N,N-dimethylaniline; phosphoniums from triethylphosphine, triphenylphosphine and diphenylphosphine; oxoniums from ethers such as diethyl ether, tetrahydrofuran and dioxane; sulfoniums from thioethers such as diethyl thioethers and tetrahydrothiophene; mixtures thereof; most preferably dimethylanilinium and mixtures thereof.

Furthermore, $[C^+]$ may be an abstracting moiety that is capable of reacting with a transition metal catalytic precursor resulting in the transition metal cation. Acceptable abstracting moiety include but are not limited to silver, carbocations, tropylium, carbeniums, ferroceniums and mixtures thereof; preferably carboniums and ferroceniums and mixtures thereof; and most

preferably triphenyl carbenium. The [C⁺] may also include mixtures of the Bronsted acids and the abstracting moiety species.

[N] is selected from the group consisting of boron, phosphorus, antimony or aluminum and mixtures thereof, having the n valence state. Preferably, the [N] is boron, aluminum and mixtures thereof.

[Q₁-Q_{n+1}] are independent, wherein Q₁-Q_{n+1} are RX is defined wherein X is a halogen group element and is typically fluorine, chlorine, and bromine and mixtures thereof; preferred halogens are fluorine, chlorine, iodine and mixtures thereof; and most preferred is fluorine; and R is mono or multi-cyclic, halosubstituted and non-substituted aryls, alkyls, and alkenyl groups and mixtures thereof; preferred are C1-20 alkenyl groups (such as ethene, propylene, butene, and pentene); C1-20 alkyl groups (such as a methyl, ethyl, n-propyl, isopropyl, n-butyl, n-octyl, and 2-ethylhexyl groups), C6-20 aryl group (including substituted aryls) (such as phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6 dimethylphenyl, 3,5- methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl groups) and mixtures thereof. More preferred R groups are C1-5 alkyls, C2-5 alkenyls phenyl and naphthyl and mixtures thereof.

26

Preferred RX compounds are C1-20 halogenated hydrocarbon groups such as XCH_2 , X_2CH , X_3C , $C_2X_nH_{n-5}$ (where $n = 1-5$), $C_3H_nX_{n-7}$ ($n = 1-7$) and $C_6X_nH_{n-6}$ ($n = 1-6$) and mixtures thereof; most preferably, FCH_2 , CHF_2 , F_3C , and fluorosubstituted phenyl, wherein the phenyl can be mono to pentasubstituted (such as p-fluorophenyl, 3,5-difluorophenyl, pentafluorophenyl, 3,4,5-trifluorophenyl, and 3,5-bis(trifluoromethyl)phenyl groups) and mixtures thereof; of these the most preferred is pentafluorophenyl.

Moreover, in this RX, the Q_1 to Q_n may be hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, substituted hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl- and halocarbyl-substituted organometalloid radicals. Additionally, the Q_1 to Q_n can simply be the X alone; for example as in BX_4 .

In addition, neutral $N^0(Q_n)$ can be used in place of the $[C^+][N^-(Q_1-Q_{n-1})]$, for example $B(C_6F_5)_3$.

Preferred $[N^-(Q_1-Q_{n-1})]$ are selected from the group consisting of $BPhenyl$, $B(C_6H_2(CF_3)_3)_4$, $B(C_6H_5)_4$, $AlPhenyl$, $Al(C_6H_2(CF_3)_3)_4$, $Al(C_6H_5)_4$, PF_6 , BF_4 , $B(OPh)_4$ and mixtures thereof; preferably $B(C_6F_5)_4$.

$\text{Al}(\text{C}_6\text{F}_5)_3$, $\text{Al}(\text{C}_6\text{H}_2(\text{CF}_3)_3)_3$, $\text{Al}(\text{C}_6\text{H}_5)_3$, $\text{BC}_6\text{H}_2(\text{CF}_3)_3$, and mixtures thereof; most preferred are $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Al}(\text{C}_6\text{F}_5)_3$ and mixtures thereof. Preferred $\text{N}^n(\text{Q}_n)$ from the neutral species of the preferred list above of $[\text{N}^n(\text{Q}_1-\text{Q}_{n-1})]$.

5 The preferred catalytic activators, when not a Lewis acid such as MgCl_2 is present, are the alkylalumoxanes and the borate activators in combination with an alkylating agent such as TEAL.

10 Catalytic systems incorporating the present invention are useful to polymerize olefinic materials, particularly ethylene. Polymerizations of olefinic monomers can be accomplished by a number of well known techniques by having the olefinic material come into contact with the polymerization catalyst(s) in a reaction
15 zone under appropriate conditions.

 As used herein, "Polymerization" includes copolymerization and terpolymerization and the terms olefins and olefinic monomer includes olefins, alphaolefins, diolefins, strained cyclic olefins,
20 styrenic monomers, acetylenically unsaturated monomers, cyclic olefins alone or in combination with other unsaturated monomers. While the catalyst system of the present invention is active for this broad range of olefinic monomer feedstock, alpha-olefin polymerizations

is preferred, especially the homopolymerization of ethylene and propylene or the copolymerization of ethylene with olefins having 3 to 10 carbon atoms.

"Polymerization techniques" for olefin

5 polymerization according to the present invention can be solution polymerization, slurry polymerization or gas phase polymerization techniques. Method and apparatus for effecting such polymerization reactions are well known and described in, for example, Encyclopedia of
10 Polymer Science and Engineering published by John Wiley and Sons, 1987, Volume 7, pages 480-488 and 1988, Volume 12, pages 504-541. The catalyst according to the present invention can be used in similar amounts and under similar conditions to known olefin polymerization
15 catalyst.

Typically, for the slurry process, the temperature is from approximately 0 degrees C to just below the temperature at which the polymer becomes soluble in the polymerization medium. For the gas phase process, the
20 the temperature is from approximately 0 degrees C to just below the melting point of the polymer. For the solution process, the temperature is typically the temperature from which the polymer is soluble in the reaction medium up to approximately 275 degrees C.

The pressure used can be selected from a relatively wide range of suitable pressures, e.g., from subatmospheric to about 350 Mpa. Suitably, the pressure is from atmospheric to about 6.9 Mpa, or 0.05-10 Mpa, especially 0.14-5.5 Mpa. In the slurry or particle form process, the process is suitably performed with a liquid inert diluent such as a saturated aliphatic hydrocarbon. Suitably the hydrocarbon is a C4 to C10 hydrocarbon, e.g., isobutane, heptane or an aromatic hydrocarbon liquid such as benzene, toluene or xylene. The polymer is recovered directly from the gas phase process or by filtration or evaporation from the slurry process or evaporation from the solution process.

The catalyst of the present invention are particularly suited for the gas phase or slurry process.

The compositions according to the present invention are used in amounts sufficient to cause polymerization in the feedstocks. Typically, the amount used will be the range of 0.0005 mmole to 10 mmole/liter of reactor; most preferably from 0.01 mmole to 2.5 mmole/liter of reactor.

The following examples are provided to illustrate the present invention, but are not to be construed as limiting the invention in any way except as provided in the appended claims.

Example A

Silica oxide carrier having a particle size of 50 μ , surface area of 300 m²/g and a pore volume of about 1.6 ml/g, such as Sylopol[®] 948, (10g, previously calcined at 800°C for 4 hours) was slurried in 100 ml of hexanes under an atmosphere of purified argon and cooled to 0°C. And TiCl₄ (16 mmol) was added and mixed for 15 minutes at 0°C. The slurry was degassed under vacuum briefly and TMS-Cp (16 mmol) was added. The slurry was mixed an additional 30 minutes. After warming to RT, the slurry was mixed an additional 2 hours. The solid was dried in vacuo.

Example B

Silica oxide with MgCl₂, having a particle size of 50 μ , surface area of 300 m²/g and a pore volume of about 1.6 ml/g, (10g) such as Sylopol[®] 5550 (10g, a GRACE Davison product containing approximately 1.6 mmol MgCl₂ per gram of support) was slurried in 100 mL of hexanes under an atmosphere of purified argon and cooled to 0°C. And TiCl₄ (16 mmol) was added and mixed for 15 minutes at 0°C. The slurry was degassed under vacuum briefly and TMS-Cp (16 mmol) was added. The slurry was mixed an

31

additional 30 minutes. After warming to room temperature, the slurry was mixed an additional 2 hours. The solid was dried *in vacuo*.

5

Example C

A 2 L Zipperclave® reactor was charged with heptanes (500 mL) and MAO (5 mmol). The reactor was pressurized with ethylene to 180 psig and the temperature equilibrated at 75°C. Example A (50 mg) was blown into the reactor under argon pressure. Polymerization was carried out for 1 hour and was quenched by rapid venting of monomer followed by methanol. The polymer, 7g, was washed with methanol and dried more than 12 hours in a vacuum oven at 60°C.

15

Example D

A 2 L Zipperclave® reactor was charged with heptanes (500 mL) and MAO (5 mmol). The reactor was pressurized with ethylene to 180 psig and the temperature equilibrated at 75°C. Example B (50 mg) was blown into the reactor under argon pressure. Polymerization was carried out for 1 hour and was quenched by rapid venting of monomer followed by methanol. The polymer, 106g, was

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washed with methanol and dried more than 12 hours in a vacuum oven at 60°C.

Example E

5 A 2 L Zipperclave® reactor was charged with heptanes (500 mL) and TEAL (2 mmol), no MAO was used. The reactor was pressurized with ethylene to 180 psig and the temperature equilibrated at 75°C. Example B (50 mg) was blown into the reactor under argon pressure.

10 Polymerization was carried out for 1 hour and was quenched by rapid venting of monomer followed by methanol. The polymer, 128g, was washed with methanol and dried more than 12 hours in a vacuum oven at 60°C.

 This example illustrates that the metallocene according can be activated without MAO in the presence of

15 a Lewis acid support material, e.g. MgCl₂.

Table

Carrier	Transition M	Si/Sn Cmpd	Activator
Silica-200°C	TiCl ₄	Cp-TMS	[DMAH] [BF ₂₀]
Silica-400°C	ZrCl ₄	Cp-TMS	[DMAH] [AlF ₂₀]
Silica-MgCl ₂	TiCl ₄	Ind-TMS	TNOA
Silica-Alumina 600°C	TiCl ₄	Cp-TBS	[DMAH] [BF ₂₀]
PVA	ZrCl ₄	Cp-SiMe ₂ Cl	BF ₁₅
Silica-Titania 600°C	ZrCl ₄	en(IndTMS) ₂	[DMAH] [BF ₂₀]
Silica-600°C	TiCl ₄	Ind-TBS	MAO
Silica-600°C	ZrCl ₄	Ind-TMS	[Ph ₃ C] [BF ₂₀]
Silica-800°C	TiCl ₄	Cp-TMS	[DMAH] [BF ₂₀]
Alumina	TiCl ₄	Ind-TMS	[DMAH] [BF ₂₀]
Titania	TiCl ₄	Cp-SiMe ₂ Cl	[DMAH] [BF ₂₀]
APG	ZrCl ₄	Cp-SiMe ₂ Cl	[DMAH] [BF ₂₀]
Silica-Titania- Chromia	ZrCl ₄	Cp-TMS	[DMAH] [BF ₂₀]
APG	HfCl ₄	Ind-TBS	[DMAH] [BF ₂₀]
Silica-Alumina	TiCl ₄	en(IndTMS) ₂	[DMAH] [BF ₂₀]
PVA	Zr(CH ₂ Ph) ₄	Cp-SiMe ₂ Cl	[DMAH] [BF ₂₀]
Alumina	TiCl ₄	en(IndTMS) ₂	MAO
Silica-800°C	TiCl ₄	Ind-TBS	[DMAH] [BF ₂₀]
Alumina-MgCl ₂	ZrCl ₄	Ind-TMS	TEAL
Silica-ZnCl ₂	ZrCl ₄	Cp-TBS	TNOA
Silica-600°C	TiCl ₄	Cp(TMS) ₂	[DMAH] [BF ₂₀]
APG	TiCl ₄	Ind-TMS	[DMAH] [AlF ₂₀]
Silica-Alumina	ZrCl ₄	Cp-TBS	TNOA
PVA	ZrCl ₄	Cp(TMS) ₂	[DMAH] [BF ₂₀]
Alumina	TiCl ₄	Cp-TBS	[DMAH] [BF ₂₀]
Talc	TiCl ₄	Ind-TMS	[DMAH] [BF ₂₀]
	TiCl ₄	Cp-TBS	[DMAH] [AlF ₂₀]

Clay, such as Montmorollinite			
Talc	TiCl ₄	Cp-TMS	[DMAH] [BF ₂₀]
Starch	TiCl ₄	Cp-TMS	[DMAH] [BF ₂₀]
Silica-Magnesia	HfCl ₄	Cp-TBS	MAO
Silica-Magnesia	TiCl ₄	Cp(TMS) ₂	[DMAH] [BF ₂₀]
Silica-600°C	Zr(CH ₂ Ph) ₄	(CpTMS) ₂ Mg	MAO
Silica-600°C	Ti(NMe ₂) ₄	Mg[Cp(TMS) ₂] ₂	MAO
Silica-600°C	HfCl ₄	2-MeInd-TMS	MAO
Silica-600°C	TiCl ₄	2-MeInd-TMS	BF ₁₅ /TEAL

APG = aluminum phosphate gel

PVA = polyvinylalcohol

WE CLAIM:

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1. A method for forming a supported polyolefin catalyst, said method comprising the steps of reacting a composition containing a transition or rare earth metal, capable of causing polymerization of olefinic materials and a metal containing reagent of the formula CM' wherein, C is selected from the group comprising a five-member carbon ring, a heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi cyclic moieties capable of coordinating to the transition or rare earth metals; and

M' is a metal selected from the group comprising tin, silicon, germanium and mixtures thereof; and a hydroxyl containing support material.

15

2. The method of claim 1, wherein the method further comprises the step of the CM' reagent further defined a component selected from the group comprising halogen elements, halosubstituted and non-substituted alkoxy, alkyl, alkenyls, and organic component that contains a five-member carbon ring, a heterosubstituted five-member carbon ring, or a bridged ligand defined as multi-cyclic moieties capable of coordinating to the transition or rare earth metals and mixtures thereof.

36

3. The method of claim 1 wherein the support is selected from the group inorganic, inorganic oxides and organic materials containing hydroxyl groups and mixtures thereof.

4. The method of claim 1 wherein the support is selected from the group comprising MgCl(OH) , Mg(OH)_2 , talcs, clays and metal oxides from the Groups 2-14, actinide, lanthanide series metals from the Periodic Table, polyvinylalcohol, starches and mixtures thereof.

5. The method of claim 1 wherein CM' is selected from the group comprising (chlorodimethylsilyl)(3-trimethylsilyl) cyclopentadiene, cyclopentadienyltrimethylsilane, indenyltrimethylsilane, indenyltributylstannane, indenyltrimethylgermanium, cyclopentadienyl trimethylgermanium, and mixtures thereof.

20

6. The method accordingly to claim 1, wherein the reaction of the CM' reagent and the hydroxyl containing support takes place in the presence of a non-polar organic solvent.

7. The method accordingly to claim 6, wherein the organic solvent is selected from the group comprising aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, petroleum fractions and mixtures thereof.

8. The method accordingly to claim 7, wherein the organic solvent is selected from the group comprising butane, isobutane, pentane, isopentane, hexane, octane, decane, dodecane, hexadecane, octadecane, cyclopentane, methylcyclopentane, cyclohexane, decalin cyclooctane, norbornane, ethylcyclohexane, benzene, chlorobenzene, xylene, toluene, gasoline, kerosene, light oils and mixtures thereof.

15

9. The method according to claim 1, wherein in the transition or rare earth containing component is represented by the formula MZ, wherein M is selected from the group comprising of Groups 3 through 10, lanthanides, actinides series metals of the Periodic Table; and Z is selected from the group comprising halogens, halosubstituted and nonsubstituted C1-C20 alkoxys, alkenyls and alkyls, C6-C20 aryls, and amides.

10. The method according to claim 9 wherein the M is selected from the group of metals comprising titanium, zirconium, hafnium, chromium, vanadium, samarium, neodymium and mixtures thereof; and Z is selected from the group comprising chlorine, fluorine, bromine, halosubstituted and non-substituted methoxy, ethoxy, isopropoxy, butoxy, pentoxy, ethyl, butyl, octyl, ethylhexyl, phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl, ethenyl, propenyl, butenyl, pentenyl, and amides of the formula NR^aR^b , wherein the R^a and R^b can be the same or different and independently selected from the group of C1-C20 alkyls and alkyls and C6-C20 aryls and mixtures of two or more of the foregoing.

11. The method according to claim 1 wherein the CM' is selected from the group comprising (chlorodimethylsilyl)(3-trimethylsilyl) cyclopentadiene, cyclopentadienyltrimethylsilane, indenyltrimethylsilane, indenyltributylstannane, indenyltrimethylgermanium, cyclopentadienyl trimethylgermanium, and mixtures thereof.

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12. The method according to claim 1, wherein the reaction mixture further contains reagent A which is selected from the group comprising acid halides, organic
5 halides, halosubstituted and non-substituted carboxylic acids, esters, ethers, alkylaluminums, halogen gases, Grignard reagents, alumoxanes and mixtures thereof.

13. The method according to claim 12 wherein A is
10 selected from the group comprising CH_3Cl , tetrahydrofuran, t-butylchloride, ethanol, phenol, ethylaluminumdichloride, silicon tetrachloride, methyl lithium, methyl magnesium chloride, triethylaluminum, methylalumoxane, dibutylphthalate and
15 tin tetrachloride, and gases of chlorine, fluorine and bromine and mixtures of two or more of the foregoing.

14. A composition of matter prepared by any of the methods of Claims 1-13.

20

15. A polymer prepared by exposing a monomeric and/or comonomeric material to the catalyst composition prepared in accordance with claims 1-13 in the presence of a catalytic activator in a reaction zone.

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16. A polymer prepared by exposing a monomeric and/or comonomeric material to the catalyst composition prepared in accordance with claims 1-13 in the presence of a catalytic activator selected from the group
- 5 comprising trimethylaluminum, triethylaluminum, diethyl aluminumhydride, triisobutylaluminum, tridecyl aluminum, tridodecylaluminum, diethyl aluminum methoxide, diethyl aluminum ethoxide, diethyl aluminum phenoxide, diethyl aluminum chloride, ethyl aluminum dichloride, methyl
- 10 diethoxy aluminum and methyaluminoxane.

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17. A polymer prepared by exposing a monomeric and/or comonomeric material to the catalyst composition prepared in accordance with claims 1-13 in the presences of a catalytic activator selected from the group of
5 compounds represented by the formula $[C']^-[N^+(Q_1-Q_{n+1})]$ and $N^+(Q_n)$,

wherein,

C+ is selected from the group of ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-
10 methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, methyldiphenylamine, pyridine, p-bromo-N,N,-dimethylaniline, p-nitro-N,N-dimethylaniline; phosphoniums from triethylphosphine, triphenylphosphine and diphenylphosphine; oxoniums from
15 ethers such as diethyl ether, tetrahydrofuran and dioxane; sulfoniums from thioethers such as diethyl thioethers and tetrahydrothiophene;

and abstracting moieties selected from the group comprising silver, carbocations, tropylium, carbeniums,
20 ferroceniums and mixtures thereof; preferably carboniums and ferroceniums and mixtures of two or more of any of the foregoing;

42

[N] is selected from the group consisting of boron, phosphorus, antimony or aluminum and mixtures thereof, having the n valence state; and

[Q₁-Q_{n+1}] are independent, wherein Q₁-Q_{n+1} are RX

- 5 wherein each of the Q in the coordinating anion may be the same or different, where in RX is defined where X fluorine, chlorine, and bromine and mixtures thereof and R is mono or multi-cyclic, halosubstituted and non-substituted C6-C20 aryls, C1-C20 alkyls, and C1-C20
- 10 alkenyl groups and mixtures thereof; and R may be hydride radicals, bridged or unbridged dialkylamido radicals, alkoxide and aryloxy radicals, substituted hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals and hydrocarbyl- and halocarbyl-substituted
- 15 organometalloid radicals and mixtures of two or more of the foregoing.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.
PCT/US 95/14363

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/602

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 546 690 (NIPPON OIL CO LTD) 16 June 1993 see page 13; example I see page 11; example D see pages 15-16; example H' see page 18; example 1 see claims 1,4-6	1,3,5-16
Y	EP,A,0 585 512 (FINA) 9 March 1994 see examples 1-3,14 see claims 1-11	1,3-16
Y	DATABASE WPI Derwent Publications Ltd., London, GB; AN 93047482 & JP,A,04 085 306 (MITSUBISHI PETROCHEMICAL) see abstract	1,3-16

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

18 March 1996

Date of mailing of the international search report

03 APRIL 1996

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INTERNATIONAL SEARCH REPORT

national application No.

PCT/US 95/ 14363

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 2
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

Claim n. 2 is incoprehensible

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter national application No

PCT/US 95/14363

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-546690	16-06-93	JP-A- 5132518	28-05-93
		JP-A- 5132519	28-05-93
		CA-A- 2082678	13-05-93
		US-A- 5331071	19-07-94

EP-A-585512	09-03-94	NONE	
